Short communication

Reversible aging behavior of $La_{0.8}Sr_{0.2}MnO_3$ electrodes at open circuit

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HIGHLIGHTS

▶ Aging behavior of LSM changes between 700 °C and 800 °C.
▶ Aging behavior is a mixture of reversible and irreversible changes in impedance.
▶ Reversible changes explained by reverse in cathode cation segregation behavior.
▶ Irreversible changes explained by microstructural changes of porous cathode.

ARTICLE INFO

ABSTRACT

$La_{0.8}Sr_{0.2}MnO_3$ (LSM) electrodes on yttria-stabilized zirconia (YSZ) electrolytes were characterized at open circuit by impedance spectroscopy. An initial irreversible change in the polarization resistance is observed for cells aged with no prior current activation. After the initial break-in, the polarization resistance rises with time at 700 °C and decays at 800 °C, reversibly, over repeated temperature cycles. The initial irreversible break-in and subsequent reversible cycling behavior suggests multiple processes happening within the time and temperatures measured. The authors propose that these processes are (1) changes in the wetting behavior of the LSM on the YSZ and (2) the reversible segregation/desegregation of cations within LSM. Between 700 °C and 800 °C, there is a transition temperature at which the segregation behavior of cations to the cathode surface changes. These measurable changes in the impedance behavior of LSM indicate that cation segregation, while considered by some to be part of the cathode activation process, may be dictated by thermodynamic factors, and thus not strictly dependent on the passage of current through the cathode.

1. Introduction

Lanthanum strontium manganite (LSM) and yttria-stabilized zirconia (YSZ) remain the most popular materials for composite cathodes in solid oxide fuel cells (SOFCs) because of their demonstrated stability. The activation of LSM/YSZ cathodes and LSM electrodes under current flow is well-documented [1–13]. Even a brief pulse of cathodic current causes a dramatic reduction in the polarization resistance of both LSM electrodes and LSM/YSZ composite cathodes. Following the electrochemical activation, the polarization resistance slowly increases at open circuit [7]. Hypotheses on the origins of the electrochemical activation are succinctly summarized by Backhaus-Ricoult et al.: "changes in the bulk defect chemistry under polarization (redox reactions of the catalyst transition metal), changes in cathode morphology and resulting improved interfacial contact under current, redistribution of impurities under current or changes in perovskite surface chemistry" [1].

We report here a reversible change, over the course of hours, in the polarization resistance of LSM electrodes on YSZ electrolytes when the temperature is cycled between 700°°C and 800 °C at open circuit with no prior current activation. The reversible changes are observed after an initial irreversible rise and decay of polarization resistance.

2. Experimental results

The reversible aging behavior was first noticed on a commercial electrolyte-supported button cell (NexTech Hionic™ electrolyte) composed of a 50 μm Ni-GDC/Ni-YSZ multi-layer anode, a 150 μm zirconia-based electrolyte, and a 50 μm LSM/LSM-GDC multi-layer cathode (Fig. 1). The cell was aged at 750 °C and then 850 °C at open
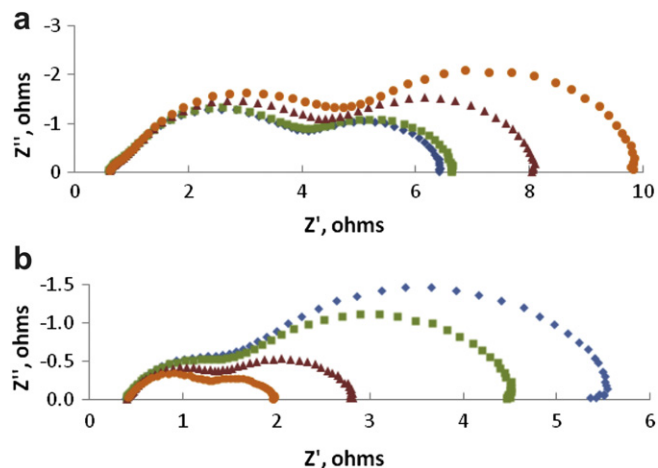
Fig. 1. Nyquist impedance plots for a NexTech Hionic™ electrolyte-supported fuel cell aged at (a) 750 °C for 1 h (diamonds), 5 h (squares), 26 h (triangles), and 53 h (circles), and (b) 850 °C for 1 h (diamonds), 5 h (squares), 26 h (triangles), and 76 h (circles). The anode fuel composition was UHP H_2 (3% H_2O), and the cathode enivronment was air.

circuit with the anode exposed to UHP hydrogen (with 3% H_2O) and the cathode exposed to air. Over a period of 72 h, the polarization resistance (defined by the difference between the high and low frequency intercepts of the impedance plots) almost doubled at 750 °C, whereas at 850 °C, the polarization decreased by more than half. Heating a similar sample directly to 850 °C showed a similar decrease in polarization resistance with time, while subsequent aging at 750 °C revealed an increase in polarization resistance. Cycling the sampling between the two temperatures always produced a growing resistance at 750 °C and a shrinking resistance at 850 °C.

The aging behavior is readily observable in symmetrical cells with LSM or LSM/YSZ electrodes exposed to air, and is most apparent on pure LSM cathodes. In these experiments, the cells are coated with gold paste current collectors and characterized by cyclic voltammetry and impedance spectroscopy using a Solartron Cell Test system. Fig. 2 illustrates the initial changes as a freshly-made symmetrical cell (Fuel Cell Materials) is exposed inside a tube furnace to 700 °C, then 800 °C, and finally 850 °C in air. The polarization resistance rises relatively rapidly and then decays slowly at 700 °C. The decay continues at the higher temperatures and appears to be more rapid at 800 °C. (The sensitivity of polarization resistance to thermal history has been observed previously [14].) This break-in period is then followed by reversible changes in the polarization resistance behavior as the temperature is cycled
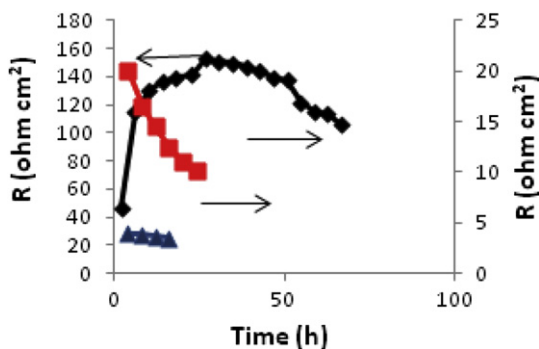
between 700 °C and 800 °C (Fig. 3). The polarization resistance consistently rises with time at 700 °C and decays at 800 °C. A plot of log($|Z|$) and phase vs. log(f) for the beginning and end of a single temperature (700 °C) shows that the aging effects occur at the lowest frequencies (data not shown). Similar behavior is observed in symmetrical cells constructed in-house.

3. Discussion

The inter-cycle decrease in the polarization resistance shown in Fig. 3 indicates an irreversible change occurring in the cell. In order to remove transient effects, a freshly-made LSM/YSZ commercial symmetrical cell (Fuel Cell Materials) was first aged for 500 h at 800 °C, and then cycled between 700 °C and 800 °C as before (Fig. 4). The results show that reproducible polarization resistances can be obtained over five temperature cycles, suggesting that stable thermodynamic states are obtained after 48 h at 700 °C and at 800 °C.

Any mechanism explaining these behaviors must account for the reversible changes in the polarization resistance behavior that occur between 700 °C and 800 °C and the overall irreversible decrease observed during the first few thermal cycles. Both processes occur on the time scale of hours and mainly affect low frequency behavior. (The activation of LSM cathodes by current flow exhibits similar behavior over similar time scales [8].) The present observations argue against strictly the formation and consumption of oxide ion vacancies in the LSM lattice, a process with a time scale of minutes at most [8]. Cation migration, by contrast, is a relatively slow process in LSM.

Cation migration may result from microstructural changes, formation of secondary phases, and redistribution of cations within the perovskite lattice. Very compelling results on microstructural changes as a cause of non-stationary behavior in LSM come from
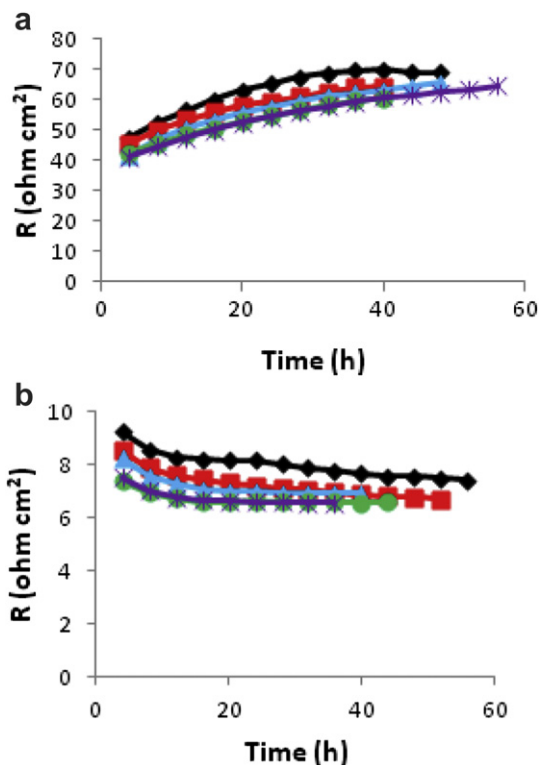

Fig. 3. Polarization resistances of the cell in Fig. 2 at (a) 700 °C and (b) 800 °C during temperature cycles 1 (diamonds), 2 (squares), 3 (triangles), 4 (circles) and 5 (asterisks).
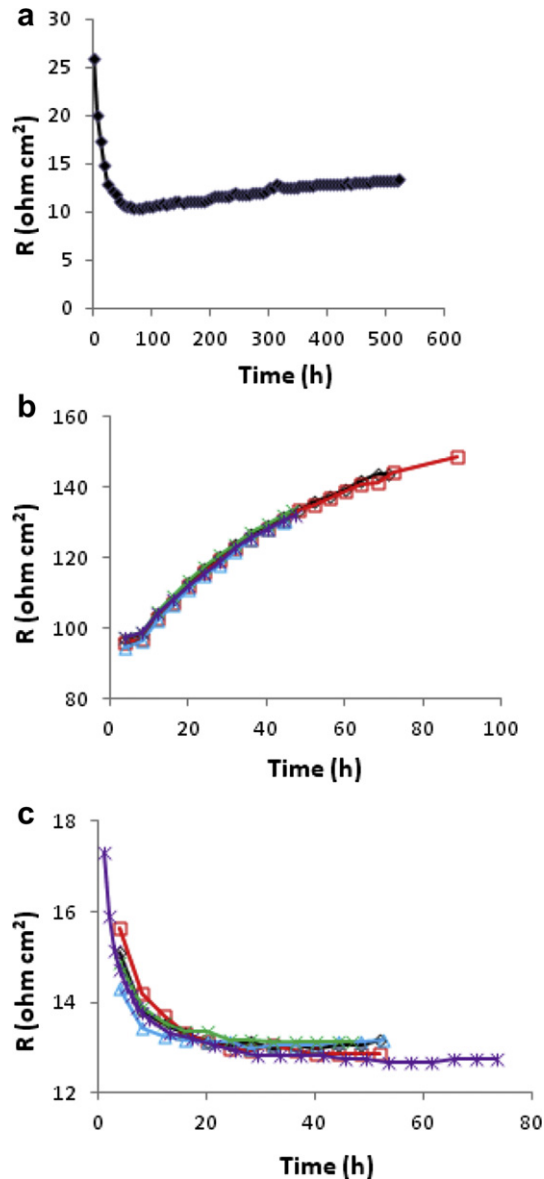

Fig. 2. Initial polarization resistances of an LSM/YSZ/LSM symmetrical cell in air at 700 °C (diamonds − left axis), 800 °C (squares − right axis), and 850 °C (triangles − right axis).

Strontium enrichment of the surface of LSM perovskites has been well-documented using a variety of techniques: Auger electron spectroscopy (AES) [15], total reflection x-ray fluorescence (TXRF) [16,17], x-ray photoelectron spectroscopy (XPS) [1,18,19], various methods of soft x-ray spectroscopy [20], and chemical analysis of an LSM surface etched by an acid solution.[3,13] Similar enrichment of the Sr:La ratio was reported with the perovskite $La_{0.6}Sr_{0.4}CoO_3$ (LSC) by Kubicek et al. using time-of-flight secondary ion mass spectroscopy (ToF-SIMS) on an LSC thin film as well as chemical analysis of the LSC surface etched by an acid solution [21]. Most literature reports demonstrate a change in the degree of strontium enrichment that depends on the thermal history of the sample. Of particular significance to the present work are results of Fister et al. [16] and Chang et al. [17], both of whom demonstrate a decrease in surface strontium enrichment as the temperature of dense LSM films increases from 300 °C up to 900 °C.

Other literature reports on cation segregation in LSM tend to contradict the strontium enrichment hypothesis described above. Caillol et al. found strontium enrichment in a screen-printed LSM layer sintered at 1200 °C for 2 h, with a return to a stoichiometric ratio of La:Sr after subsequent aging at 800 °C for one week, suggesting an opposite trend as that of Fister et al. and Chang et al. [18] However, as the segregation of cations would seem preferable at lower temperatures (as dictated by the positive entropy of mixing), it seems plausible that the driving force for strontium enrichment would decrease with increasing temperature, barring any other secondary phase formation. Ia O' et al. reported surface lanthanum enrichment of LSM as analyzed by AES and XPS under conditions of very high cathodic polarization (on the order of −5 V) [22].

The appearance of a maximum and minimum in the polarization resistance shown in Figs. 2 and 4(a), respectively, indicates that more than one process occurs during the transitory (irreversible) phase of the aging experiments. We propose that these processes are (1) the breaking up of the LSM at the LSM/YSZ interface caused by changes in the wetting behavior of the LSM on the YSZ surface, along with (2) the segregation of cations toward and from the surfaces and/or interfaces of LSM. At sintering temperatures, LSM will tend to wet the surface of YSZ, while cation segregation will be suppressed. When temperatures are brought to a level well below that of sintering, cracks begin to form in the LSM film formed by the wetting process (alternatively, reverse-wetting could take place), thereby increasing the TPB length and decreasing the resistivity. Simultaneously, cation segregation (possibly strontium) from the bulk of the LSM toward the free surfaces and interfaces occurs, which increases the polarization resistance. The temporally dominant term depends on the temperature and the relative activation energies of these processes, along with other factors such as the specific stoichiometry, morphology and thermal history of the cell. Such a picture is consistent with the appearance of a resistivity maximum in one cell tested at 700 °C, and a minimum in a different cell tested at 800 °C.

4. Conclusion

We propose that cation segregation (leading to a secondary phase or otherwise) is responsible for the reversible changes between 700 °C and 800 °C shown in Figs. 3(a)–(b) and 4(b)–(c). This designation was made primarily because of the fact that wetting of YSZ by LSM has not been observed at temperatures below 800 °C, and because of the fact that an increase in wetting (which is associated with higher polarization resistance) would tend to occur at higher temperatures, whereas we observe a decrease in resistance at the higher temperature.

This hypothesis implies that cation segregation to the surfaces and/or interfaces in LSM is a thermodynamic − not just a kinetic −

Fig. 4. (a) Polarization resistance of an LSM/YSZ/LSM symmetrical cell during a 522 h soak at 800 °C. (b) Polarization resistances of the cell at 700 °C. (c) Polarization resistances of the cell at 800 °C. In (b) and (c), the temperature cycles are indicated by 1 (diamonds), 2 (squares), 3 (triangles), 4 (circles) and 5 (asterisks).

Woo et al., who showed that the temperatures used during sintering can cause LSM particles to "melt" and spread across the YSZ interface [10]. The LSM films produced in the Woo experiments exhibited poor cathode performance until they were exposed to reducing conditions. The reducing conditions purportedly cause cracking (or reverse-wetting) of the LSM film, thereby increasing the TPB length.

Early evidence for cation redistribution (or possibly secondary phase formation) at the LSM-air interface was reported by Jiang, who showed that when fresh LSM electrodes are etched with HCl solution prior to initial polarization measurements, the initial polarization resistance is reduced, and the change in polarization resistance with cathodic current activation is less than that of an unetched LSM electrode [8]. The etchant solution in Jiang's experiment contained much higher concentrations of La and Sr and lower concentrations of Mn than predicted by the molar composition of the LSM.

phenomenon, which is in accord with the results of Fister et al. [16] This hypothesis does not necessarily rule out the role of kinetic demixing of cations under an electric field in explaining some burn-in behavior in LSM/YSZ cathodes [23–25]; however, it does introduce another possibility: the burn-in phenomenon under polarization is a thermodynamically-driven response to electrochemically-induced $p(O_2)$ changes in the cathode. As lowering the cell operating temperature would increase the driving force for cation segregation, the amount of polarization required to reverse this segregation should increase at lower temperatures. For low cathodic overpotentials, some degradation in cell power may still occur due to cation segregation, depending on the operating temperature. This degradation would thus need to be accounted for in modeling long term performance or off peak hour cycling (when cells may be held at open circuit or lower overpotentials for long periods of time).

While these results have been repeated with multiple symmetrical cell samples and electrolyte-supported button cells, they are the initial results from more aging experiments with different cathode and electrolyte compositions with post-mortem surface analyses currently in progress. Further, the effect of cathodic overpotential on this reported aging effect needs to be determined.

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